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(54) Title: SIMULATED COLORED GRANITE AND PROCESS

(57) Abstract

Simulated granite in selected colors with increased levels of alumina trihydrate (ATH) and decreased amounts of preground ATH-filled polymer particles of selected colors, and preparative process.

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SIMULATED COLORED GRANITE AND PROCESS

Background of the Invention

This invention relates to simulated colored granite and its production, using filler of alumina trihydrate (ATH) in syrup and pre-ground particles of ATH-filled polymer.

This is an improvement for making simulated granite articles with colors other than black and white over U.S. Patents 4,085,246 (1978) and 4,159,301 (1979), both to Buser, Roedel and Vasilliou. U.S. Patent 3,775,364 (1973) - Duggins, describes casting and polymerization systems useful in the present invention. All three of these patents are hereby incorporated herein by reference.

U.S. Patent 4,544,584 - Ross (1985) describes technology for making simulated stone products including colorants.

Summary of the Invention

The present invention provides a preparative process and a simulated granite article comprising

A. 60 to 99% by weight (based on weight of the article) of a matrix comprising

(1) 30 to 45% by weight (based on weight of the article) of methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, and

(2) 30 to 60% by weight (based on weight of the article) of alumina trihydrate particles having a maximum particle size less than

about 100 microns in the longest dimension;

B. 0.8 to 20% by weight (based on weight of the article) particles in the size range of 100 to 800 or 2000 microns comprising a matrix of methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, filled with (based on the weight of the particles) 50 to 70% by weight alumina trihydrate and up to 2.5% by weight pigment, having a clear to white color;

C. 0.1-10% by weight (based on weight of the article) of particles in the size range of 100 to 2000 microns comprising a matrix of methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, filled with (based on the weight of the particles) 0.1-2.5% pigment having a black color;

D. 0.1-10.0% by weight (based on weight of the article) of particles in the size range of 100 to 2000 microns comprising a matrix of methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, filled with (based on the weight of the particles) 0.1-2.5% pigment of selected color other than black and white; and

E. 0-1% by weight (based on the weight of the article) of pigments of selected colors in at least the matrix of A.

Detailed Description

In order to provide simulated granite articles with colors other than black and white and desirable aesthetics more economically, it has been discovered that the ATH content of the matrix should be increased above that normally used and to a particular narrow range within the general teachings of related art, while the content of ATH-filled particles should be decreased and appropriate pigments added to the particles. Optionally, the matrix can be pigmented at low levels. Since the particles can be more costly than the matrix resin, this permits cost savings.

Desirable sand-colored simulated granite can be made using brown and yellow pigmented particles, and pink to rose colored simulated granite can be made using red pigments in the particles. Similar pigments can be used in the matrix.

The content of ATH in the matrix is increased from a normal level near 30% to the range of 30 to 60%, preferably 45 to 55%. All parts, percentages and proportions are by weight, based on the weight of the article, except where indicated otherwise. Percentages of filler in pre-ground particles are by weight based on the weight of the particles themselves.

The content of pre-ground particles in the article preferably is down from a normally used 33% to 5-20%, more preferably at least about 10%. These changes, surprisingly, permit significant improvement in aesthetics with sustained physical, chemical and mechanical properties.

In the following examples and comparative test, formulations are presented which are processed as in the above-cited Buser et al patents and others known in the art to produce useful end product in the

form of flat sheet and shape such as kitchen sinks and bowls. The seive size series used are in the American Standard Sieve Series in which 25-50 mesh is 700-300 microns and 50-100 mesh is 300 to 150 microns.

The particles are preformed methyl methacrylate polymer (PMMA) filled with about 62 to 65% by weight ATH particles and comminuted by techniques known in the art, preferably cryogenically, to the indicated mesh sizes, which are all in the range of 100 to 800 microns. The total filler level is also indicated, showing how much ATH plus pre-ground particles are in the matrix syrup. Suitable pigments known in the art can be used.

The comparative test gave acceptable results but in different color families, black and white rather than sand or rose. For obtaining the colors other than black and white, the present invention is particularly useful.

Example 1

Sand Color	Particle Size	Wt% in Final Product
Filler		
ATH in matrix	35 microns	47.0
White particles (1% TiO_2)	25-50 mesh	2.0
	50-100 mesh	8.0
White particles (0.1% TiO_2)	25-50 mesh	4.0
Black particles (1% pigment)	25-50 mesh	0.5
Brown particles (0.7% pigment)	25-50 mesh	2.0
	50-100 mesh	1.0
Yellow particles (1% pigment)	50-100 mesh	0.5
Total filler level		65.0
PMMA matrix		35.0

Example 2

Rose Color	Particle Size	Wt% in Final Product
Filler		
ATH in matrix	35 microns	43.5
White particles (1% TiO_2)	50-100 mesh	8.0
White particles (0.1% TiO_2)	25-50 mesh	12.0
Black particles (1% pigment)	25-50 mesh	0.5
	50-100 mesh	0.6
Red particles (1% pigment)	25-50 mesh	0.4
Total filler level		65.0
PMMA matrix		35.0
Background pigment		0.025

Comparative Test

Gray Color	Particle Size	Wt% in Final Product
Filler		
ATH in matrix	35 microns	29.6
White particles (1% TiO_2)	25-50 mesh	9.5
	50-100 mesh	3.2
White particles (0.1% TiO_2)	25-50 mesh	3.2
Black particles (1% pigment)	25-50 mesh	11.3
	50-100 mesh	6.3
Total filler level		63.0
PMMA matrix		37.0

Claims

1. A simulated granite article comprising

A. 60 to 99% by weight (based on weight of the article) of a matrix comprising

(1) 30 to 45% by weight (based on weight of the article) of methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, and

(2) 30 to 60% by weight (based on weight of the article) of alumina trihydrate particles having a maximum particle size less than about 100 microns in the longest dimension;

B. 0.8 to 20% by weight (based on weight of the article) particles in the size range of 100 to 2000 microns comprising a matrix of methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, filled with (based on the weight of the particles) 50 to 70% by weight alumina trihydrate and up to 2.5% by weight pigment having a clear to white color;

C. 0.1-10% by weight (based on weight of the article) of particles in the size range of 100 to 2000 microns comprising a matrix of such methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with

alpha-beta-ethylenically unsaturated compounds, filled with (based on the weight of the particles) 0.1-2.5% pigment having a black color;

D. 0.1-10.0% by weight (based on weight of the article) of particles in the size range of 100 to 2000 microns comprising a matrix of such methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, filled with (based on the weight of the particles) 0.1-2.5% pigment of selected color other than black and white; and

E. 0-1% by weight (based on the weight of the article) of pigments of selected colors in at least the matrix of A.

2. The article of claim 1 in which the selected colors of the pigments of (D) are brown and yellow, and the article has an overall color similar to sand.

3. The article of claim 1 in which the selected color of the pigments of (D) is red and the article has an overall color in the range of pink to rose.

4. The article of claim 1 wherein the white pigment of B is selected from the group consisting of titanium dioxide, barium sulfate, zinc sulfide and zinc oxide.

5. The article of claim 4 wherein the white pigment includes zinc oxide or zinc sulfide.

6. A process of preparing a simulated granite article of claim 1 by:

A. preparing a matrix wet mix comprising about 60 to 99% by weight (based on the weight of the article) comprising about:

(1) 30-45% by weight (based on the weight of the article) of a syrup of 10 to 35% by weight (based on the weight of the syrup) of methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compound, the balance of said syrup being monomer of such methyl methacrylate polymer, and

(2) 30 to 60% by weight (based on the weight of the article) of alumina trihydrate particles having a maximum particle size less than about 100 microns in the longest dimension;

B. mixing with said matrix wet mix about:

(1) 0.8 to 20% by weight (based on weight of the article) particles in the size range of 100 to 800 microns comprising a matrix of methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, filled with (based on the weight of the particles) 50

to 70% by weight alumina trihydrate and up to 2.5% by weight pigment having a clear to white color;

(2) 0.1-10% by weight (based on weight of the article) of particles in the size range of 100 to 2000 microns comprising a matrix of such methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, filled with (based on the weight of the particles) 0.1-2.5% pigment having a black color;

(3) 0.1-10.0% by weight (based on weight of the article) of particles in the size range of 100 to 2000 microns comprising a matrix of such methyl methacrylate polymer selected from the group consisting of methyl methacrylate homopolymers and copolymers of methyl methacrylate with alpha-beta-ethylenically unsaturated compounds, filled with (based on the weight of the particles) 0.1-2.5% pigment of selected color other than black and white; and

(4) 0-1% by weight (based on the weight of the article) of pigments of selected colors in at least the matrix of A;

C. adding an initiator system for the polymerizable constituent;

D. introducing the composition from (C) onto a casting surface or into a mold; and

E. curing the composition to form the article.

7. The process of claim 6 wherein the white pigment of B is selected from the group consisting of titanium dioxide, barium sulfate, zinc sulfide and zinc oxide.

8. The article of claim 4 wherein the white pigment includes zinc oxide or zinc sulfide.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/03146

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 04 B 26/06, // B 44 F 9/04

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	C 04 B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, 3847865 (DUGGINS et al.) 12 November 1974 see claim 1 --	1-8
Y	US, A, 3488246 (DUGGINS et al.) 6 January 1970 see column 8, line 12 - column 10, line 50 --	1-8
A	FR, A, 2179022 (DU PONT DE NEMOURS) 16 November 1973 see claims 1,4-6,18 --	1
A	EP, A, 0211657 (NIPPON SHOKUBAI KAGAKU KOGYO) 25 February 1987 see page 11, line 8 - page 15, line 18 --	1
A	US, A, 4544584 (ROSS et al.) 1 October 1985 see column 6, line 48 - column 7, line 33 cited in the application -- ./.	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
2nd November 1989	04 DEC 1989

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	F.M. VRIJDAG

International Application No. PCT/US 89/03146

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Chemical Abstracts, volume 88, no. 12, 20 March 1978, (Columbus, Ohio, US), see page 38, abstract 75057z, & JP, A, 77129722 (NIPPON GAKKI CO., LTD) 31 October 1977	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 8903146 SA 30508

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/11/89
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